New Nitric Oxide Standards for Next-Generation Low-Emission Vehicles

Stakeholders in the American Industry/Government Emissions Research (AIGER) group are working together to facilitate the automobile industry meeting more stringent 2003 Federal Tier II and California LEV II emission regulations. AIGER members include the U.S. Environmental Protection Agency (EPA), California Air Resources Board (CARB), General Motors, Ford, and Daimler-Chrysler. NIST and the US Motor Vehicles Manufacturers have worked together since 1975 to develop sixty gaseous Standard Reference Materials (SRMs) which are the nation's benchmarks against which all EPA-mandated fuel economy and mobile source emission measurements must be traceable, by federal law. NIST currently supports AIGER members by maintaining reasonable inventories of required gas SRMs, which consist of dilute mixtures of key pollutants such as hydrocarbons, carbon monoxide, and nitric oxide.

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NIST has had a long-term relationship with the AIGER group. In 1998, NIST developed ten low NO working standards at concentrations of 500 nmol/mol, 750 nmol/mol, 950 nmol/mol, 1050 nmol/mol, and 1250 nmol/mol, which have exhibited excellent NO concentration stability for more than 5 years. These working standards are the benchmarks against which SRM 2737 (500 nmol/mol nitric oxide in nitrogen) and SRM 2738 (1000 nmol/mol nitric oxide in nitrogen) are being assigned concentration values.

In 2001, AIGER provided funding directly to a specialty gas company to gravimetrically blend 25 candidate mixtures of SRM 2737 and 25 candidate mixtures of SRM 2738. The 50 candidate SRM cylinders were then transferred to NIST to perform stability monitoring and SRM certification analyses. Each cylinder has been individually certified for NO and NO_x concentration values at an expanded uncertainty of ± 1.5% relative. NIST is currently adding these 50 certified cylinders to its listing of available SRMs.

Low-concentration gas standards are required since newer vehicles produce lower levels of pollutants. The new engines employ fuel injection with an air-to-fuel ratio optimized by on-board computers. Emissions are further reduced by more efficient catalytic converters.

During vehicle emissions testing, the tailpipe exhaust levels are diluted with clean air and collected using constant volume sampling bags or new mini-diluter technology. AIGER stakeholders have identified the need for significantly lower NIST gas standards containing carbon monoxide, hydrocarbons, and nitric oxide. The completion of SRM 2737 and SRM 2738 had been identified as their highest priority. NIST is currently exploring nitric oxide working standards below 100 nmol/mol.

NIST participated with other national metrology institutes in the Consultative Committee for Amount of Substance Key Comparison 26a (CCQM-K26a) study where each laboratory independently measured the nitric oxide concentration for their "unknown" gas sample. The Gas Metrology Group assigned a concentration of (715 ± 7) nmol/mol nitric oxide in nitrogen for the NIST test sample, referencing the suite of low-concentration NO working standards. This result agreed with the assigned concentration value determined by the CCQM Pilot laboratory for this test sample within similar levels of uncertainty.

A technical solution to the stability problems that were observed in the lowest concentration NO SRMs prepared in the 1980s and early 1990s has been developed, and AIGER members have been provided with interim standards with which to work. The project will provide two much needed lower-concentration NIST certified NO SRMs. These new SRMs will help facilitate vehicle manufacturers in meeting US EPA and CARB's current and future lower-emission regulations.

Future Plans: NIST is continuing to move NO analytical standards and measurement capability lower toward the goal of 100 nmol/mol, defined by AIGER as the next highest priority for the future. The current working standards at 1000 nmol/mol will be augmented with a new set of gravimetric primary standards prepared by the ten-fold gravimetric dilution of the current gravimetric suite. These new standards will then be verified by comparison with the NO working standards. Optimization of chemiluminescence measurements at these lower concentrations will be worked on simultaneously – eventually leading to a suite of NO working standards in the 100 nmol/mol range.